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K. W. Jones
Brookhaven National Laboratory, Upton, New York

H. Feng
Montclair State University, Upper Montclair, New Jersey

A. Lanzirotti
University of Chicago, Chicago, Illinois

N. Marinkovic
Albert Einstein College of Medicine, Bronx, New York

U. Neuhäusler and C. Riekel
European Synchrotron Radiation Facility, Grenoble, France

L. Vincze and B. Vekemans
University of Antwerp, Antwerp, Belgium

I. Szaloki
University of Debrecen, Debrecen, Hungary

Z Song
Guangzhou Institute of Geochemistry, Guangzhou, China

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K. W. Jones (jones@bnl.gov)
(Brookhaven National Laboratory, Upton, New York)
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ABSTRACT: Sediments found in the New York/New Jersey Harbor are widely contaminated with organic and inorganic compounds of anthropogenic origin. As a result, the environmental health of the Harbor has deteriorated and the efficient operation of the Port compromised by difficulties in disposing of sediments resulting from maintenance and improvements of navigational channels. Knowledge of the properties of the sediments on a micro-scale is useful in understanding the transport of contaminants through the environment, for developing effective methods for sediment decontamination, and for subsequent beneficial use of the cleaned sediments. We have investigated several properties of these sediments using synchrotron radiation techniques. These include computed microtomography using absorption and fluorescence contrast mechanisms, x-ray microscopy, microbeam x-ray fluorescence, and Fourier Transform Infrared Spectroscopy (FTIR) for measurements of microstructure, distribution of metals on individual sediment particles, and chemical forms of the contaminants on a micrometer scale. Typical results obtained with these techniques are presented.

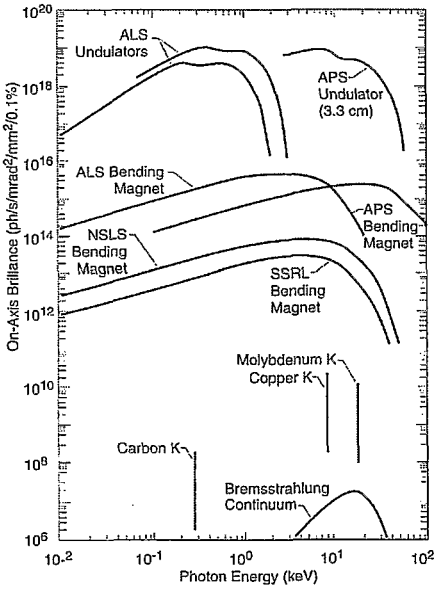
INTRODUCTION

The sediments are contaminated with harmful organic and inorganic compounds whose effects must be considered during the course of navigational dredging or environmental restoration projects. The properties of the sediments found in the New York/New Jersey Harbor vary widely from point to point in the Harbor. Describing their properties and transport on a grain-size scale (or a few-micrometer scale) is a difficult task without a high resolution analytical optical device. Conventionally, multiple samples are taken and, in some cases, composites prepared that are then analyzed using standard chemical techniques. Not surprisingly, there is a large variability in the analytical results. This type of data can be used as the basis for modeling contaminant distributions and making predictions of their transport.

An understanding of the complex biogeochemical and physical processes underlying the macro-scale phenomena is essential for gaining useful information on the transformation mechanisms and on the effects of contaminants upon the environment and related human health. This can only be achieved by making measurements on sediments at the scale of molecular to small grain sizes. There has been a recent surge of interest in

carbon K-alpha x ray absorption edge were used to discriminate between sediment particles and organic materials. Measurement of the energy dependence of the attenuation (x-ray absorption near-edge spectroscopy, XANES) was used to obtain information on the functional groups of carbon present. A hard x-ray microprobe at beam line X26A used Kirkpatrick-Baez mirrors to focus beam to a spot size of 10 μm x 10 μm with energies that could be adjusted in a range between 4 and 20 keV. Characteristic x-rays were detected with a Si(Li) x-ray detector. This beam line was used to map elemental concentrations in sediment grains and to make computed microtomography measurements in sections through individual grains. The detection limits for elements around Fe were around 500 ag. Non-destructive absorption computed microtomography experiments were carried out at beam line X27A. The equipment employed an area detector and the experiment were performed by taking a series of exposures with a CCD camera of the light from an x-ray scintillator as the target was stepped through a rotation of 180 degrees. Voxel sizes were of the order of 5 μm. Finally, spatially resolved Fourier Transform Infrared microscopy was carried out at the NSLS UV ring U2B beam line with a spatial resolution of about 15 μm. Spectra were obtained for single sediment particles and for extracts from the sediments. Schematic diagrams of the NSLS experimental apparatus are given in Figures 2-5.

Experiments at the ESRF used similar apparatus, but benefited from the higher beam intensities and energy range to make computed microtomography measurements with improved spatial resolution and x-ray mapping and XANES measurements at higher energies than could be obtained with the use of the X1A and X26a beam lines at the NSLS. The experimental equipment used at beam line ID13 for computed microtomography and for high-resolution microscopy at beam line ID21 are shown in Figures 6 and 7.



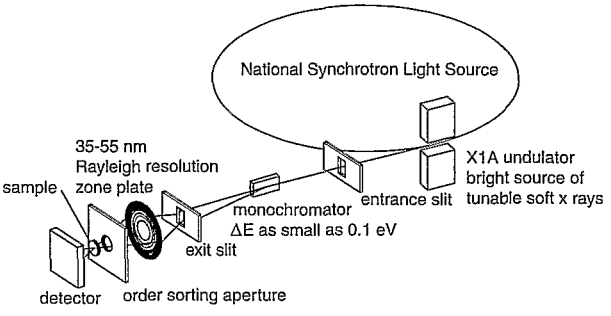


FIGURE 2. Components of the NSLS X1A x-ray microscope facility. The apparatus at the ESRF ID 21 beam line is similar.

FIGURE 1. X-ray brilliance produced at the Brookhaven National Synchrotron Light Source (NSLS) Argonne Advanced Photon Source (APS), Berkeley Advanced Light Source (ALS), the European Synchrotron Radiation Facility (ESRF), and with conventional x-ray sources.

this multidisciplinary field driven, at least in part, by the development of new analytical techniques. The use of synchrotron x-ray radiation is an example (Fenter et al., 2003; Jones et al., 2003; Neuhaeusler et al., 2003; and Vincze et al. 2002). The synchrotron source produces x-rays and infrared beams with intensities 3-4 orders of magnitude higher than those produced by conventional sources. Use of the synchrotron source has made possible new types of investigations related to environmental problems.

A large number of synchrotron-based investigations have concentrated on measurements of model systems or relatively well-defined materials. The situation for the real world on NY/NJ Harbor sediments is so complex that it is difficult to extrapolate from simpler experiments to an understanding of the larger scale. Therefore, we have chosen to investigate some of the properties of actual sediments on the small size scale so as to provide an intermediate stage between model experiments and making predictions on a macroscopic scale.

MATERIALS AND METHODS

We obtained sediment samples from a number of different locations around New York/NJ Harbor locations. A particularly useful sample was the National Institute of Standards and Technology Standard Reference Material 1944, New York/New Jersey Waterway Sediment. During preparation, the sample was sieved to remove fine particles so that 50% of the particles have a diameter less than 150 μm. Other samples investigated were surficial samples from Newtown Creek, a tributary of the East River, and from Newark Bay, New Jersey.

The Synchrotron Source. There are now almost 40 synchrotron radiation laboratories in various stages of development located around the world. Thus, there are sufficient facilities to enable their use as general purpose facilities so that it is now possible to consider these facilities as readily available tools that can be used for both basic and applied sediment-related measurements. Briefly, for those not familiar with these facilities, the synchrotron source consists of a ring of magnets that contains a high-energy electron or positron beam. As the beam traverses the circular path energy is radiated in the form of electromagnetic radiation. The radiated photons have a continuous energy spectrum from the infrared to the hard x-ray region. The exact spectrum depends on the electron energy and the radius of the electron orbit. The advantage of this source is that it can be focused to give very high fluxes beams, its continuous energy distribution so that the experimental beam energy can be tuned to specific values, and a high degree of polarization that is useful in several different types of experiments. The relation of the synchrotron source to tube-type sources is shown in Figure 1 where the beam characteristics of different sources are shown and compared to conventional laboratory sources. Our experiments were made using three experimental stations at the NSLS x-ray ring, one at the ultraviolet (UV)/infrared ring, and two stations at the ESRF.

Experimental Apparatus. At the NSLS the experiments performed used four different types of experimental apparatus. High-resolution work was carried out at the NSLS X1A beam line by measuring the amount of attenuation of the x-ray beam that was focused using a zone plate. The spatial resolution was about 100 nm. Measurements were done in an environmental wet cell on hydrated specimens. Measurements below and above the

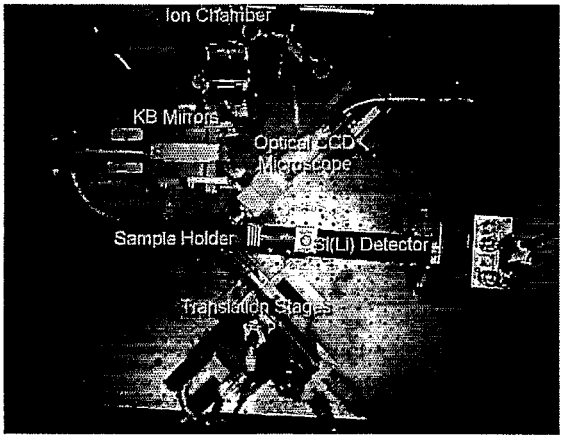


FIGURE 3. Photograph of the NSLS X26A hard x-ray microbe.

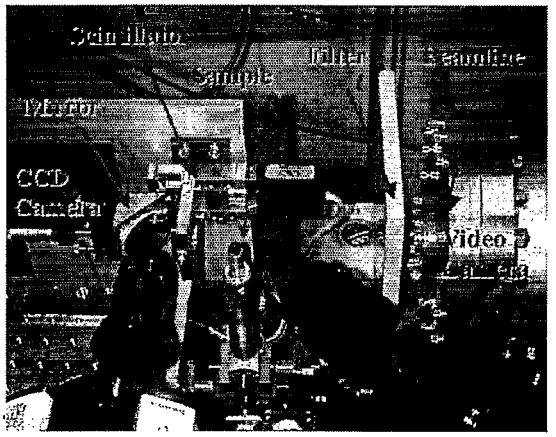


FIGURE 4. Photograph of the NSLS X27A computed microtomography apparatus.

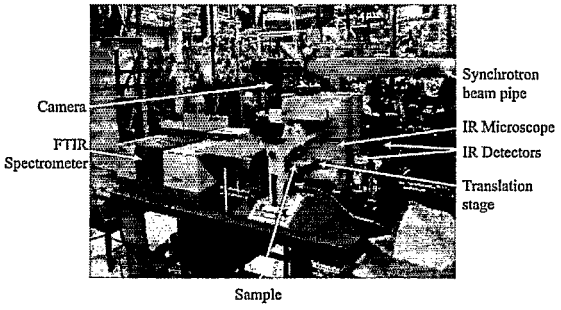


FIGURE 5. Photograph of the NSLS U2B Fourier Transform Infrared (FTIR) microscope beam line.

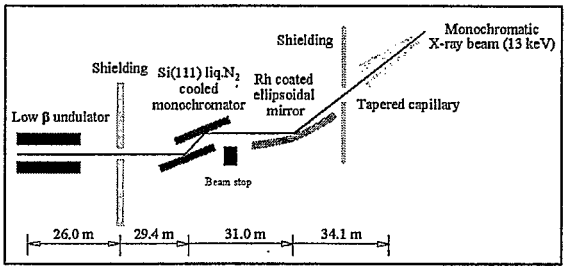
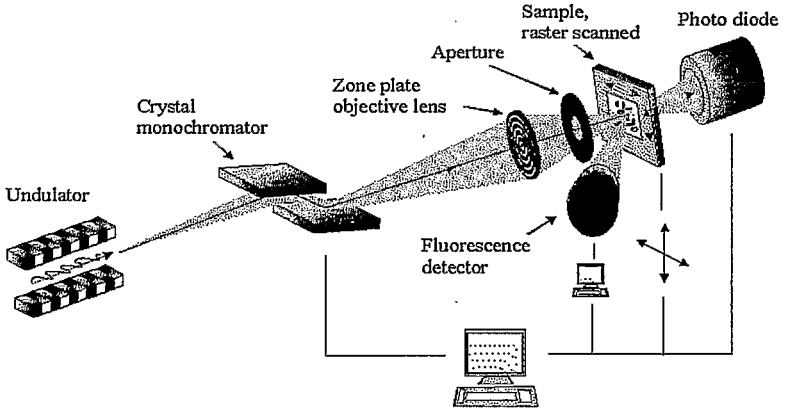


FIGURE 6. Schematic diagram of the ESRF ID13 x-ray microprobe.

FIGURE 7. Schematic diagram of the ID 21 experimental apparatus.



RESULTS AND DISCUSSION

The experiments carried out with the equipment described yielded results that are relevant to both the physical and chemical properties of the sediments. A description of the results obtained with each technology is given here.

High-resolution X-ray Radiography (NSLS X1A). Radiographic measurements of sediment particles in the micrometer size range showed the existence of organic materials that were and were not associated with clays/silts. The size of the organic materials was often many times that of the inorganic materials. Several measurements were made of the functional groups found in the organic materials using the XANES technique. The results for the physical shapes could be useful in modeling the effects of the high-pressure water jets used as a component in sediment decontamination using washing techniques. The functional groups found in several measurements showed differences between points in untreated sediments and in an organic material remaining after a sediment washing treatment. Typical results for the radiographs made below and above the carbon K-absorption edge for determining the particle structures and for the XANES scan that show the functional groups are displayed in Figure 8.

Computed Microtomography (NSLS X27A). Transport of contaminants through sediments can occur by chemical diffusion and by fluid transport driven by tidal-induced pressure changes. Physical transport of surface sediments with concomitant sedimentation is also of concern. Knowledge of the microstructure of the sediments is essential for comparison with theories of sediment formation and for application of lattice Boltzmann transport models for modeling contaminant transport in this porous medium. Tomographic results for a sample of sediment are shown in Figure 9. Here, the grain and pore volumes are easily discernible. The pore space is shown as the black regions. The various shades of gray indicate particle locations and differences in grain composition through differences in the x-ray attenuation coefficients. The voxel size for this example is 0.007 mm. Analysis of the data gives the variation of porosity through the measured volume, the different pathways through the volume, and the tortuosity of the material. Ultimately, computations that include the chemical interactions between the sediments and the contaminants transported in the liquid phase will be possible.

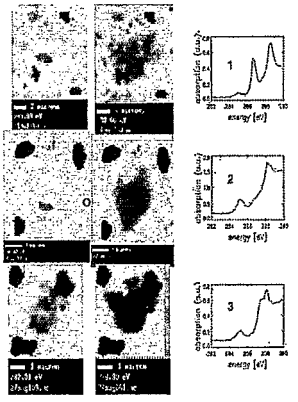


FIGURE 8. Carbon attenuation radiograph and XANES measurement from X1A.

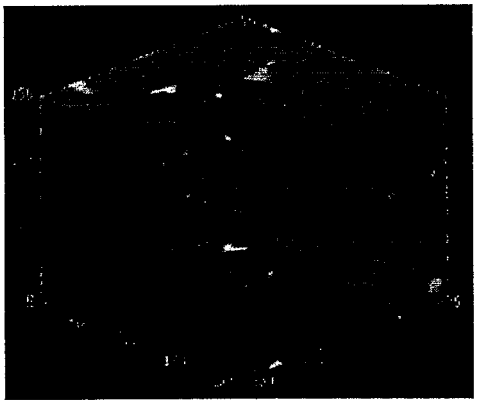


FIGURE 9. Non-destructive tomography work at X27A.

X-ray Microprobe Elemental Mapping (NSLS X26A). Maps of the elemental concentrations over individual sediment particles were made to determine variability between different particles and over single particles. The x-ray probe can detect elemental concentrations less than 1 fg in a pixel of 0.010 mm x 0.010 mm. The volume of material contribution depends on the energy of the incident x-ray beam and on the energy of the characteristic x-ray emitted following production of a inner-shell vacancy. The results of the experiment therefore represent a radiograph and not a picture of the surface concentrations. Nevertheless, it is reasonable to consider that localized concentrations may lie on the surface and that more uniform distributions could be indicative of contributions from the particle matrix. A map of the distribution of Pb concentrations over a number of sediment particles from NIST SRM 1944 is shown in Figure 10.

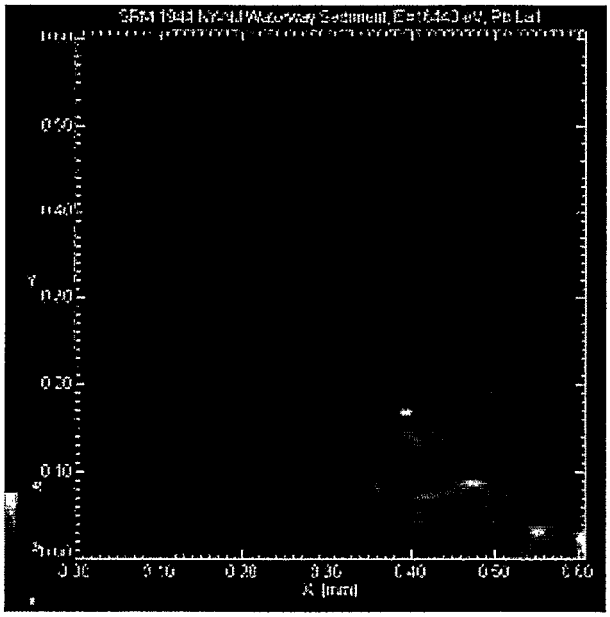


FIGURE 10. X-ray fluorescent map of lead concentrations for particles of SRM 1944

Functional Group Determination By FTIR Spectroscopy (NSLS U2B). FTIR spectroscopy with spatial resolution of 15 μm is a powerful method for determining the chemical functional groups in thin specimens of sediments or in liquids extracted from the sediments. This is illustrated in the map and spectra shown in Figure 11. The microphotograph in the upper left of the figure shows particles from a sample of Gowanus Canal (Brooklyn, New York) sediment. The dashed box shows the region of the sample investigated. The map shows the variation in intensity of the region around the C-H stretch bond at about 2800 cm^{-1}. Variations are caused by differences in organic compound concentrations and changes in the sample thickness. We have found that the peaks for the C-H bond region are excellent indicators of the presence of anthropogenic contaminants. Infrared spectra for two locations, one at the lower left of the figure, the other at the right-hand edge at the center of the map, are also presented in Figure 11. One particle is essentially pure SiO_2, while the other is rich in peaks attributed to

contamination with organic compounds. A more comprehensive analysis of the data will give a detailed picture of the variability of the composition of the material on a grain-size scale.

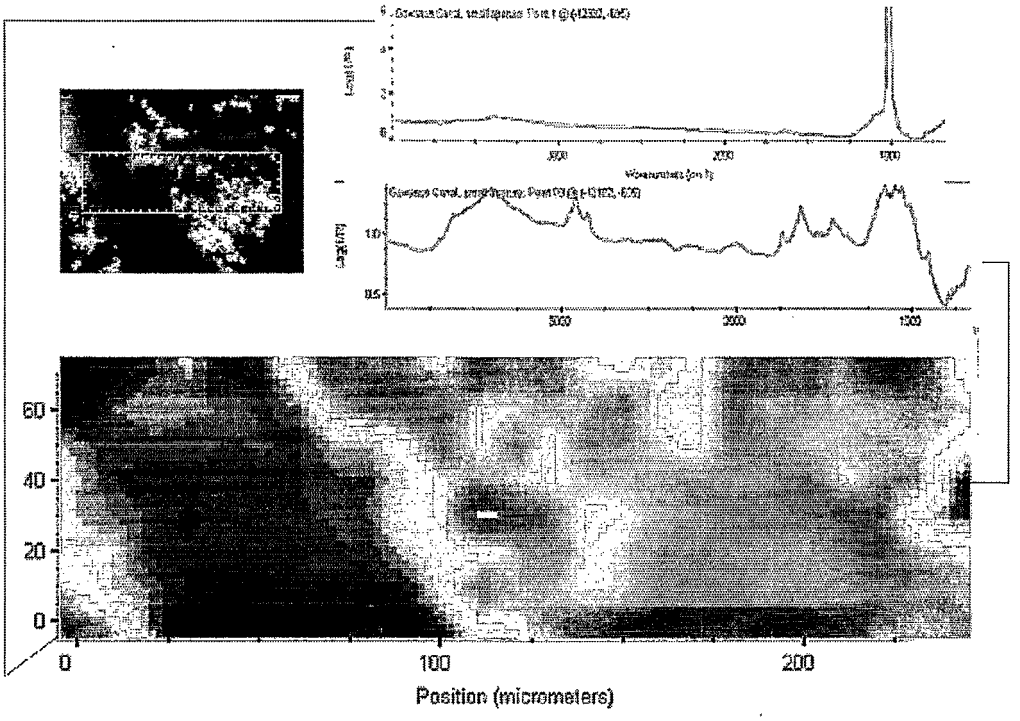


FIGURE 11. FTIR map and spectra obtained at NSLS beam line U2B. The region mapped is shown at the upper left. Further details are provided in the text.

Elemental Computed Microtomography (ESRF ID13). Elemental computed microtomography based on the detection of characteristic x rays is a non-destructive way of measuring the spatial distribution of elements in the sediment particles. Measurements with a voxel size of 0.003 mm were made on a single particle taken from New York Harbor. The results shown in Figure 12 for this particular section point to the possible existence of a composite particle. The elements do appear to be distributed throughout the section. Cr, a presumed contaminant, is not seen to be found in a shell at the periphery of the particle. Hence, the particle appears to be permeable and with toxic metals distributed in the interior. A simultaneous measurement of the x-ray diffraction could help to establish the composition of the matrix and to differentiate between low-porosity quartz material and higher porosity clay. In this case, the observation of K could point to the latter material.

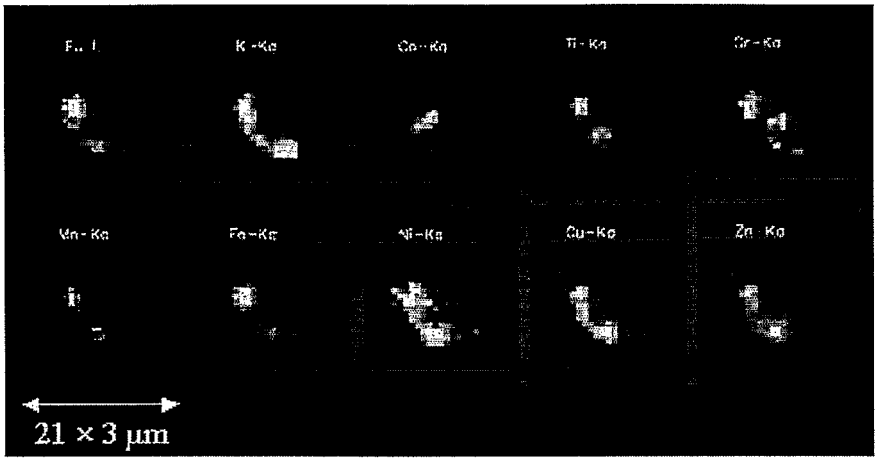


FIGURE 12. Fluorescent tomographic section obtained at the ESRF ID 13 beam line.

X-ray Microprobe Elemental Mapping (ESRF ID21). The type of measurements made at the NSLS X1A beam line were extended to higher energies at the ESRF ID21 beam line. In this case the characteristics of the ESRF synchrotron, undulator, and zone-plate focusing made possible at energies up to 8 keV. We used this beam line during two investigations. The first was made to map the distribution of S in NIST SRM 1944 particles. The second was made to look at the distribution of elements from Si to Fe. In this case, the higher beam energy made it possible to study the Cr distribution, but also reduced the sensitivity for detection of S and other lighter elements. The spatial resolutions achieved for the two runs were about 0.0005 mm. A map of the S distribution found for a single large particle is shown in Figure 13. The small circular areas with high concentrations are also found in maps of the Fe distribution. The XANES measurements shown help to define the chemical functional group found for the S. There is evidence for the possible existence of pyrite in one scan, but there is also a region where there is evidence for other functional groups. Comparison of the maps for other elements made at 8 keV fail to reveal strong correlations between their locations.

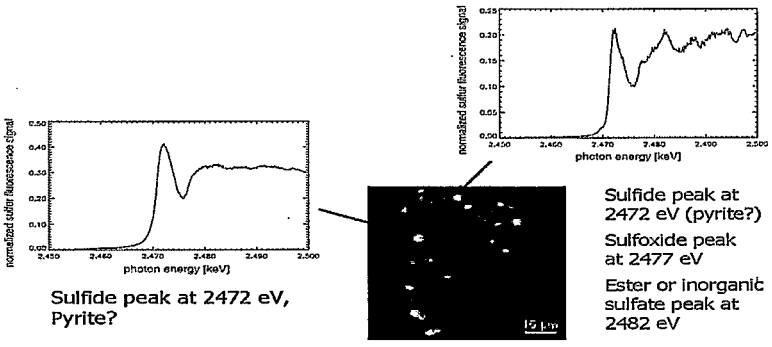


FIGURE 13. Map of S distributions on SRM 1944 grains and XANES spectra at two different points.

CONCLUSIONS

We applied different synchrotron based x-ray analytical techniques to study sediments obtained from NY/NJ Harbor. The results show that this approach is a powerful method for determining sediment properties on micrometer and sub-micrometer size scales. The experiments give information about the physical properties of the sediments that can be used as a realistic starting point for fluid flow calculations and for modeling interactions between high-pressure water jets used in washing technologies and composite organic/inorganic particles. Chemical attributes including the distribution of trace contaminants and the functional groups of organic compounds can also be found on individual particles. These results will help to clarify transport mechanisms and to assist in choice of surfactants and chelators for dealing with the removal of specific contaminants.

In the future, we hope to extend these experiments by trying to develop and strengthen the connections with simplified model experiments. Experiments that are linked to the use of natural attenuation using microbial techniques will also benefit. Finally, we expect to see rapid improvements in the synchrotron instrumentation that will further improve the sensitivity and data acquisition speeds of these experiments.

ACKNOWLEDGEMENTS

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